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(21) International Application Number: <b>PCT/GB99/02721</b> (22) International Filing Date: <b>18 August 1999 (18.08.99)</b> (30) Priority Data: 09/136,853                      19 August 1998 (19.08.98)                      US (71) Applicant (for all designated States except US): <b>METHANEX CORPORATION [CA/CA]; 1800 Waterfront Centre, 200 Burrard Street, Vancouver, British Columbia V6C 3M1 (CA).</b> (72) Inventors; and (75) Inventors/Applicants (for US only): <b>BUSH, Christopher, John, Thomson [NZ/NZ]; 40 Plympton Street, New Plymouth, Taranaki (NZ). MACDONALD, Michael, Glencoe [CA/CA]; 1591 Nanton Avenue, Vancouver, British Columbia V6J 2X3 (CA). KIRKPATRICK, Robert, Duncan [NZ/NZ]; 79 Onslow Avenue, Epsom, Auckland 3 (NZ). TURNBULL, David, McGregor [NZ/NZ]; Aspen, Marama Road, Seddon, Marlborough (NZ). JONES, Brian, Dennis [CA/CA]; 20 Oersted Street, Kitimat, British Columbia V8C 1J5 (CA). FARNELL, Peter, William [GB/GB]; 9 Riverslea, Stokesley, North Yorkshire TS9 5DE (GB).</b>		(74) Agent: <b>HOWARD, Paul, Nicholas; Carpmaels &amp; Ransford, 43 Bloomsbury Square, London WC1A 2RA (GB).</b> (81) Designated States: <b>AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CR, CU, CZ, DE, DK, DM, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).</b>  <b>Published</b> <i>With international search report.</i> <i>Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>
(54) Title: <b>METHOD FOR PERFORMING A PROCESS WHEREIN A FEEDSTOCK IS SUBJECTED TO AN ENDOTHERMIC REACTION</b>  (57) Abstract <p>A process wherein a feedstock is subjected to an endothermic reaction, particularly a catalytic reaction, and particularly a process for reforming a feed comprising a gaseous mixture of hydrocarbons and steam which is passed at an elevated pressure over a catalyst to produce reformed gas containing hydrogen and carbon oxides, the heat required for the endothermic reaction being supplied by heat exchange with a flow of hot combustion products generated by burning a fuel in a pressurized oxidant flow in a combustion zone thereby particularly cooling said flow of combustion products, and thereafter recirculating part of the partially-cooled flow of combustion products by adding said part to said pressurized oxidant flow before said oxidant flow enters said combustion zone; and apparatus therefor.</p>		

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METHOD FOR PERFORMING A PROCESS WHEREIN A FEEDSTOCK IS  
SUBJECTED TO AN ENDOTHERMIC REACTION

BACKGROUND OF THE INVENTION

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Field of the Invention

This invention relates to a new or improved method for performing a process wherein a feedstock is subjected to an endothermic reaction, particularly a reforming process, and apparatus therefor, which are useful, *inter alia*, in the production of methanol and other synthesis gas products, and to a novel process and apparatus which facilitates the construction of large capacity methanol plants, and/or plants where space and or weight limitations may apply and where conventional combustion systems may not be appropriate.

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Description of the Prior Art

It has long been appreciated that methanol, otherwise known as methyl alcohol, can be produced from natural gas (and also from other hydrocarbon deposits such as oil and coal or biomass). Methanol is a basic building block for a variety of petrochemical and fuels products.

The conventional methanol production process from natural gas involves a reforming process wherein feedstock that comprises a mixture of natural gas and steam in a controlled ratio, typically 1.0 to 4.0 moles of steam per gram atom of hydrocarbon carbon in said natural gas, is subjected, at an elevated pressure, typically in the range 10 to 80 bar gauge, to elevated temperatures over a catalyst to produce a reformed gas that consists of a mixture of hydrogen, oxides of carbon, steam and some residual methane. Such reforming is typically performed by passing the natural gas/steam mixture through a reforming catalyst, usually nickel on a suitable support, disposed in tubes which are heated so that the reformed gas leaves the catalyst at a temperature of the order of 850 to 950°C. The reformed gas is then cooled to condense the excess of

steam and the water is separated to give a de-watered gas suitable for use as synthesis gas for methanol synthesis. The reforming reaction is endothermic and requires the combustion of a fuel or other energy input to provide the necessary heat. In an alternative process, commonly referred to as autothermal reforming, the reformed gas is produced using partial combustion with essentially pure oxygen of the  
5   aforementioned feedstock. Combined reforming is also practised using a combination of the above two reforming processes. The synthesis gas is then pressurized to the desired synthesis pressure, which is typically in the range 50 to 120 bar gauge, for example about 80 bar gauge, and passed over a copper catalyst to synthesize methanol  
10   which is subsequently purified through a distillation process if high purity methanol is required. The methanol synthesis is often effected in a loop wherein the synthesis gas, together with unreacted gas, is passed through the synthesis catalyst, methanol is separated from the resultant gas leaving unreacted gas which is recycled. Part of the unreacted gas is purged from the loop as purge gas to prevent a build up of inerts in the  
15   loop.

The high temperatures involved in the reforming process and the high pressure involved in the synthesis process result in methanol plants being expensive to construct and difficult to operate.

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In many conventional, autothermal or combined reforming processes the hot reformed gas which exits the reformer typically passes through a waste heat boiler for raising high pressure steam. The raising of high pressure steam introduces many potential problems and costs to the methanol plant not the least of which are the  
25   equipment costs of the steam plant and the cost of providing the chemicals needed to treat the boiler feedwater. Prior art steam reforming processes are described inter alia in U.S. 4,337,170 Fuderer and U.S. 5,039,510 Pinto.

In conventional methanol plants the feedgas is typically passed over catalyst in  
30   vertical tubes which are arrayed within a furnace operating essentially at atmospheric pressure with burners where suitable fuel (typically natural gas and/or purge gas) is burned in the presence of air. The tubes are heated by radiation and convection,

predominantly by radiation, to apply the required heating to the feedgas in the tubes. In large scale conventional methanol production plants such a reforming section becomes excessively large and imposes a practical limit on the capacity of such plants to less than 1.5 million tonnes per year.

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### SUMMARY OF THE INVENTION

It is the aim of the present invention to provide a new or improved method for performing a process wherein a feedstock is subjected to an endothermic reaction, particularly a catalytic reaction and particularly a reforming process, together with apparatus for carrying out such process.

Accordingly, the invention provides a process wherein a feedstock is subjected to an endothermic reaction, particularly a catalytic reaction, with heat required for the endothermic reaction being supplied by heat exchange with a flow of hot combustion products, generated by burning a fuel in a pressurized oxidant flow in a combustion zone, thereby partially cooling said flow of combustion products, and thereafter recirculating part of the partially-cooled flow of combustion products by adding said part to said pressurized oxidant flow before said pressurized oxidant flow enters said combustion zone.

In particular, the invention provides a process for the reforming of a feedstock comprising a gaseous mixture of hydrocarbons and steam by applying heat thereto to carry out the endothermic reforming reaction at an elevated pressure over a catalyst to produce reformed gas containing hydrogen and carbon oxides; wherein said heat is generated by burning a fuel in a pressurized oxidant flow in a combustion zone to yield a flow of hot combustion products, and using said flow of hot combustion products in a reforming stage to heat said feedstock and provide reaction heat thereby partially cooling said flow of combustion products, and thereafter recirculating part of the partially-cooled flow of combustion products by adding said part to said pressurized oxidant flow before said pressurized oxidant flow enters said combustion zone.

Recycle of part of the flow of partially-cooled combustion products enables the temperature of said flow of hot combustion products to be moderated.

As used herein the expression "pressurized oxidant flow" is defined to mean a  
5 flow of gas or gases pressurized to a pressure above atmospheric pressure comprising at least oxygen or a mixture of oxygen with nitrogen, wherein the oxygen content can be greater than, equal to, or less than the oxygen content of atmospheric air.

The invention will hereinafter be described with reference to a reforming  
10 process. However, the general principles and features described are also applicable to the supply of heat to any process in which a feedstock is subjected to an endothermic reaction, particularly a catalytic reaction. In particular, the aspects of the invention relating to the recirculation of combustion gases, as well as more generally applicable features and parameters of the process and apparatus herein described, are also  
15 applicable to any process in which a feedstock is subjected to an endothermic reaction, particularly a catalytic reaction.

In the present invention, the recirculated part of the flow of combustion products is mixed with the pressurized oxidant flow before the latter has passed through  
20 the combustion chamber or zone, e.g. a burner. The process of the present invention is advantageous over a process in which the partially-cooled combustion products are added to the gas flow exiting the combustion zone, as discussed below.

Typically, in conventional processes in which a feedstock is subjected to an  
25 endothermic reaction, and particularly reforming processes, the temperature of the combustion products exiting the combustion zone is around 2000°C. The recycling of the flow of the partially-cooled combustion products in order to moderate the temperature of the flow of hot combustion products exiting the combustion zone can attenuate the temperature of the latter to below about 1600°C and desirably to between  
30 about 1200°C to 1400°C. It is important, however, that the temperature of the flow of combustion products passed to the reformer to provide the reaction heat is uniform. If the temperature is not uniform then some portions of the apparatus (e.g. the tubes in the

reformer) will be exposed to higher temperatures, which will result in higher operating temperatures and lower tube lifetimes. Furthermore, it is known that non-uniform temperature in a feed stream to a heat-exchange device leads to a reduction in the amount heat transferred within that device.

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In a process in which the flow of partially-cooled combustion products is added to the flow of hot combustion products exiting the combustion zone, it is therefore important to ensure intimate mixing of the two flows so that a uniform temperature of gases within the flow is attained. In such a process, the mixing device must be designed to contain gases at a temperature around 2000°C, which requires expensive materials of construction. High-efficiency metallic mixers could not be used for this operation and mixing could normally only be achieved using jet-mixing based on the momentum of the two flows. In addition, the burners in the combustion zone in such a process must be designed to contain gases at a temperature of around 2000°C and would also require the use of expensive materials for their construction.

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In the process of the present invention the partially-cooled combustion products are added to the pressurized oxidant flow prior to combustion of the fuel in the combustion zone. This mixing occurs at lower temperatures, typically between about 300°C and about 800°C. At such temperatures commercially available metallic mixers, such as helical static mixers, may be used. Furthermore, the addition of the partially-cooled combustion products to the pressurized oxidant flow means that the maximum temperature in the combustion zone can be maintained below about 1600°C. Accordingly, a process according to the present invention is economically advantageous in that it would enable the apparatus to be constructed from lower-cost materials. In addition, because a high degree of mixing between the partially-cooled combustion products and the pressurized oxidant flow may be achieved, the temperature of the gases in the flow exiting the combustion zone is highly uniform. Accordingly, the temperature of the flow passed to the reformer is more uniform than that of a flow produced by recycling the partially-cooled combustion products directly to the flow exiting the combustion zone. Consequently, the lifetime of other components in the reformer apparatus would be extended.

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The process of the present invention provides further benefits in that a lower combustion temperature results in the formation of lower levels of pollutants, such as nitrogen oxides, in the flow stream. Finally, mixing of the partially-cooled combustion products upstream of the combustion zone would provide advantages over mixing downstream of the combustion zone in situations where there is only a limited amount of space available between the combustion zone and reformer. Such situations may arise, for example, in the case of very large capacity plants in which the reformer vessel may be of large diameter and incorporated with the combustion chamber into a single vessel.

The above described arrangement conserves the residual heat of the recirculated part of the combustion products flow which adds significantly to the thermodynamic efficiency of the process. The temperature of the recycled, i.e. recirculated, part of the flow of combustion products (which has been partially cooled during passage through the reforming stage as a result of supplying heat for the endothermic reforming reaction) is set by an optimization between the desire for high temperature to improve the thermodynamic efficiency and the more expensive and complex mechanical equipment that is necessary for operation at higher temperatures.

By pressurizing the combustion system, a much greater flow of heat per unit volume can be achieved, and therefore for a given level of heat flow and heat transfer in the reformer apparatus, a much more compact arrangement can be utilized as compared to prior art systems. An important aspect of the current invention is a compact process with an improved process efficiency. This enables the fabrication of large capacity plants (in the case of methanol, for example, in excess of 1 million Tonne/yr methanol) which has up to now been regarded as close to the limiting capacity of conventional non-oxygen reforming technology in single stream plants.

Preferably the combustion system operates at a pressure in excess of 10 bar gauge, and more preferably in excess of 15 bar gauge. A pressure in the range of 10 to 40 bar gauge is considered optimum, although advantages are likely to be realized at



pressure levels from 10 to 60 bar gauge, and even a range of 5 to 80 bar gauge. It is preferred that the combustion system operates at a pressure that is not more than 10, preferably 5, bar above or below the reforming pressure. In this way large pressure differentials across the walls of the vessel, e.g. tubes, separating the flow of hot combustion products from the feedstock undergoing reforming are avoided, thus  
5 reducing metallurgical problems.

While a reforming process with a pressurized combustion system without recirculation of a portion of the hot combustion gas is technically feasible, such a  
10 process suffers from higher cost and reduced efficiency. These two disadvantages make this scheme economically unattractive.

By recirculating a portion of the combustion products flow after it has been used to heat the reformer, it is possible to moderate the hot combustion gas temperature  
15 in a safe and effective manner. It is noted that the flame temperature of natural gas and/or purge gas burned in air can be of the order of 2000°C whereas the temperature of the hot combustion products is attenuated to a level between about 1000°C to 1600°C, desirably between about 1200°C to 1400°C, by recirculation of a portion of the combustion products. This lower combustion products temperature adds  
20 significantly to the operability of the reformer system and helps to mitigate the potential for equipment damage resulting from process upsets. It is known that the combustion products' temperature in conventional reforming systems can be attenuated by adding excess air to the burner so that a resultant temperature of the combustion products in the desired range of 1000°C to 1600°C, preferably 1200°C to 1400°C can  
25 be achieved. However the oxygen present in this excess air supply can cause problems since if an oversupply of fuel to the burner should accidentally occur, the oxygen in the excess air will burn the extra fuel so that instead of the combustion products temperature being moderated, it can become excessive and may cause widespread damage to the apparatus system. In contrast, with the present invention this problem  
30 does not occur since the recirculated combustion product flow is practically inert (typically having an oxygen content of less than 2%, particularly less than 1%) so that the temperature moderating effect is still achieved regardless of any oversupply of fuel.

In a preferred embodiment of the invention, the proportion of the combustion products that is recycled is 5 to 80%, particularly 30 to 70%, of the total amount of combustion products leaving the combustion zone (i.e. recycled combustion products plus fresh combustion products).

In an alternative embodiment, the proportion of the combustion products that is recycled is such as to provide a flow of hot combustion products having a temperature within a range of from about 1000°C to about 1600°C, preferably from about 1200°C to about 1400°C.

In a further embodiment of the invention, the relative amounts of pressurized oxidant gas and fuel provided to the combustion zone is such that the hot combustion products exiting the combustion zone have an oxygen content of less than about 5%, preferably less than about 2% and particularly less than about 1%.

In a further preferred embodiment of the invention, the reforming is effected in two stages comprising a first stage wherein the feedstock is partially reformed by the application of heat thereto and a second stage wherein the partially reformed feedstock delivered from the first stage is further and more completely reformed by the application of heat, with heat in at least the second stage being supplied by said pressurized flow of hot combustion products. The reformed gas from the second stage can be utilized to effect heating of the feedstock in the first reforming stage, or alternatively this heating of the first reforming stage can be done by utilizing the hot combustion products.

In an alternative arrangement, the feedstock is divided into two portions. One portion is reformed in a reforming stage heated by the hot combustion products as aforesaid, while the other portion is reformed in a parallel reforming stage wherein the heat is supplied as described below. The reformed gas from the two reforming stages is combined and then subjected to partial combustion with a pressurized oxidant gas and optionally passed through a bed of a secondary reforming catalyst. The resultant hot

reformed gas is then used to provide the heat in the parallel reforming stage. In this embodiment, it is preferred that the pressurized oxidant gas used for the partial combustion is oxygen or oxygen-enriched air. In this case, the oxidant gas used for the partial combustion may be obtained by subjecting compressed air to separation in a  
5 membrane unit and the residual oxygen-depleted air from the air separation unit may be re-pressurized as necessary and used as the pressurized oxidant gas used to form the hot combustion products.

Preferably some or all of the partially-cooled flow of combustion products that  
10 is not recycled to the pressurized oxidant flow is delivered to an expander machine where useful work is recovered by expanding said portion to a lower pressure and temperature. This useful work can be applied to many purposes, one preferred purpose being to effect pressurization of the oxidant flow that is delivered to the combustion zone. The work can also be used for other compression duties, for example and  
15 without limitation, to recycle compression, synthesis gas compression, and synthesis gas circulation.

In a further aspect, the invention provides an apparatus for performing a process in which a feedstock is subjected to an endothermic reaction, particularly a catalytic  
20 reaction, said apparatus comprising: an endothermic reaction zone; means to deliver the feedstock into said endothermic reaction zone; means to supply a heating medium to said endothermic reaction zone to effect said endothermic reaction; a combustion zone; means for delivering to said combustion zone a flow of pressurized oxidant gas and a supply of fuel; means for burning said fuel in said pressurized oxidant flow in said  
25 combustion zone to produce a hot flow of pressurized combustion products; means for delivering said hot flow of combustion products to said endothermic reaction zone for use as the heating medium therein; and means for recirculating a portion of said flow of combustion products after passing through said endothermic reaction zone to said flow of pressurized oxidant gas before said flow of pressurized oxidant gas enters said  
30 combustion zone.

In another aspect, the invention provides an apparatus for the reforming of a feedstock comprising a gaseous mixture of hydrocarbons and steam by applying heat thereto to carry out endothermic reaction over a catalyst to produce reformed gas containing hydrogen and carbon oxides, said apparatus comprising: a reforming zone; means to deliver the feedstock into said reforming zone; means to supply a heating medium to said reforming zone to effect reforming of said feedstock; a combustion zone; means for delivering to said combustion zone a flow of pressurized oxidant gas and a supply of fuel; means for burning said fuel in said pressurized oxidant flow in said combustion zone to produce a hot flow of pressurized combustion products; means for delivering said hot flow of combustion products to said reforming zone for use as the heating medium therein; and means for recirculating a portion of said flow of combustion products after passing through said reforming section to said flow of pressurized oxidant gas before said flow of pressurized oxidant gas enters said combustion zone.

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In a preferred embodiment of the invention the means for recirculating the partially-cooled flow of combustion products comprises an eductor.

#### BRIEF DESCRIPTION OF THE DRAWINGS

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One form of the invention will further be described, by way of example only, with reference to the accompanying drawings wherein:

Figure 1 is a block diagram illustrating the overall process and system of apparatus in accordance with the invention for the production of methanol;

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Figure 2 is a schematic diagram of the reformer section and pressurized combustion circuit.

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Figure 3 is a diagram showing the eductor component in accordance with a preferred embodiment of the invention.

Referring to Figure 1, a pressurized natural gas feed 10 (if necessary treated to remove sulphur species and other contaminants to render it suitable for reforming over conventional nickel catalysts) is mixed with water, which may be supplied as steam, through a line 54 to achieve a controlled ratio of water to hydrocarbon carbon in the reforming feedstock. The feedstock at a temperature of about 250°C is delivered to a preheater 13 wherein it is heated to a temperature of about 450°C before being delivered for two-stage reforming in a pre-reformer (CXP) 14 and a final reformer (CXR) 15. In the pre-reformer 14 and in the reformer 15 the feedstock is passed at high temperatures over nickel or other pre-reformer or reformer catalysts and is thereby reformed to produce the reformed gas, the heat required for the reforming step being produced by a pressurized combustion circuit 18. The reformed gas is cooled by passing through a cooler 16 which constitutes a heat exchanger in which heat is delivered to the preheater 13, and then further cooled, and water condensed and separated, prior to the resultant de-watered synthesis gas being passed to a compressor 17 where it is compressed to a pressure of approximately 80 bar gauge before being delivered to the synthesis section 19 wherein the reformed feedstock is converted into methanol. From the synthesis section 19 the product is delivered to a distillation section 20 wherein the methanol is separated by a distillation process.

The reforming section of the process is more fully illustrated in Figure 2, particularly in relation to the pressurized combustion circuit 18. Pressurized feedstock which has been heated to a temperature of about 450°C in the preheater 13 is delivered over catalysts retained in tubes 24 (for clarity, only one of which is shown in Figure 2; in practice there may be tens or hundreds of such tubes) in the compact exchange pre-reformer (CXP) 14. The feedstock is typically at a pressure in the range of about 20 to 50 bar gauge. The heat required to drive the endothermic pre-reforming reaction is supplied on the shell-side of the pre-reformer by hot reformed gas delivered from the compact exchange reformer (CXR) 15 through line 25. The reformed gas in the line 25 is at a temperature of about 750°C and is cooled in the pre-reformer 14 to a temperature of about 500°C, and is further cooled in the preheater 13 to a temperature of about 300°C before being delivered through line 26 to the downstream portions of the process indicated at 27 in Figure 2. Tubes 24 have a set of central tubes 24a disposed axially

within tubes 24 for the passage of the partially reformed gas from tubes 24 to line 28. As the partially reformed gas flows along the central tubes 24a it cools, providing part of the heat required for the reforming reaction, leaving tubes 24a and passing to the reformer (CXR) 15 through line 28.

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Partially reformed feedstock, now at a temperature of about 600°C, is passed from the pre-reformer 14 through a line 28 to the reformer 15 wherein the feed gas is again passed over a second catalyst retained in tubes 30 (for clarity, only one of which is shown in Figure 2; in practice there may be tens or hundreds of such tubes). The reformer 15 acts in a manner analogous to a heat exchanger, the heat to support the endothermic reforming reaction within the tubes 30 being supplied on the shell side of the reformer 15 by a flow of controlled hot combustion products delivered through a line 31 from the pressurized combustion circuit 18 as shown in Figure 1. Within the heated tubes the feed gas is heated to a temperature of about 900°C at the bottom of tubes 30, substantially completing the reforming reactions. Tubes 30 have a set of central tubes 30a disposed axially within tubes 30 for the passage of the fully reformed gas from tubes 30 to line 25. As the fully reformed gas flows along the central tubes 30a it cools, providing part of the heat required for the reforming reaction, leaving tubes 30a at a temperature of about 750°C and passing to the pre-reformer (CXP) 14 through line 25.

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The two stage reforming process described in the foregoing has several advantages. Primarily it ensures that high efficiency is achieved by exchanging heat from the reformed gas leaving the (CXR) 15 directly to supply both the heat required for endothermic reforming in the pre-former (CXP) 14, and also the heat delivered in the pre-heater 13.

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The pressurized combustion circuit 18 as shown in Figure 2 comprises a burner or combustor 34 that is supplied with a pressurized fuel comprising a combination of natural gas via line 35, and further combustible gas (such as purge gas, which contains an excess of hydrogen, from the methanol production process 27) delivered through line 36. The combustion circuit 18 operates at a high pressure, typically in the range of

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15 to 40 bar gauge and preferably at a pressure differing from that of the pressurized feedstock by no more than 10 bar, and at such pressures produces a high density flow of combustion products that is delivered through the line 31, with the result that for a given output of reformed gas the reformer (CXP 14 and CXR 15) can be very much smaller and more compact than would have been possible using a conventional unpressurized or low pressure combustion circuit. The combustor 34 can be either a separate piece of equipment or can be incorporated into the reformer vessel.

Oxidant to support the combustion process is provided in the form of air that is pressurized in a compressor 37 from which it is delivered through a line 38 to the combustor. Since the adiabatic flame temperature of the fuel when burned in the compressed air in the combustor 34 is about 2000°C to moderate the temperature of the combustion products delivered in the line 31 to the desired range of 1000°C to 1600°C, preferably 1200°C to 1400°C, an inert gas is added to the air feed via a line 39. The inert gas used comprises a portion of the combustion products which, after passing through the reformer (CXR) 15, exit from the shell side thereof through a return line 40. This stream has been partially cooled through heat exchange within the reformer 15 and can therefore be used to attenuate and control the temperature of the combustion product stream delivered through the line 31.

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The recycled combustion product stream is essentially inert, having no more than about 2%, preferably less than 1% oxygen, and therefore offers an effective and safe means for temperature control, although the recycled stream also requires some degree of repressurization to bring it to the pressure of the air feed in the line 38. This repressurization may, for example, be effected by means of a compressor 43 through which the recycled combustion product stream is directed. Although the recycled stream has been partially cooled in the reformer (CXR) 15, it is still too hot to be passed through the compressor 43, and is therefore pre-cooled by being passed through a heat exchanger 44, the heat extracted therein being largely recovered by recirculating the pressurized flow from the compressor 43 back through the heat exchanger 44 prior to its delivery to the combustor 34. Prior to passage through the compressor 43, the recycle stream is further cooled in heat exchanger 44a (not shown in Figure 2).

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In a preferred arrangement, compressor 43 and heat exchangers 44 and 44a are omitted and recycle of the part flow of partially-cooled combustion products is effected by means of an eductor wherein the flow of pressurized oxidant gas 38 is passed through a constriction, e.g. a nozzle or jet, and thence into an expansion zone, whereby a zone of reduced pressure is created. The part flow of partially-cooled combustion products is drawn into this reduced pressure zone to effect the recycle. In this arrangement, it is necessary to increase the pressure of the flow of pressurized oxidant gas to provide the motive power for the eductor. Figure 3 shows a representation of an eductor 60.

There are several advantages of using an eductor in the recirculation of the partially-cooled combustion products. Firstly, this arrangement avoids the need for compression of the flow of the partially-cooled combustion products. Secondly, the eductor can operate with moderately hot gaseous flow at temperatures up to 900°C and there is therefore no requirement to cool and reheat the flow of partially-cooled combustion products as there would be for a scheme including compressor 43. Standard compressors for this duty are typically limited to operating temperatures of around 200°C while more expensive specialist machines may operate at up to about 500°C. Accordingly, in addition to the omission of compressor 43, heat exchangers 44 and 44a may also be omitted when an eductor is used in the process of the invention. Finally, an eductor is a highly turbulent flow device that ensures very rapid and efficient mixing. Accordingly, the eductor produces a mixed gas with very little variation in temperature or composition and removes the need for a dedicated mixing component. The use of an eductor as hereinbefore described is mechanically simpler and, furthermore, has economic advantages in relation to a conventional arrangement since the cost of the incremental duty on the oxidant gas compressor plus the cost of the eductor is less than the cost of an additional compressor, heat-exchangers and mixer. In addition, the thermal efficiency of the process is also increased since more heat energy is conserved.



The remainder of the partially-cooled combustion products delivered to the line 40 is passed to an expander 42 which is coupled to drive the compressor 37. In expander 42 this remainder of the partially cooled combustion products is expanded to a lower temperature and pressure with the recovery of a large amount of useful work  
5 which is sufficient to drive the compressors 37 and 43 (if used) as well as contribute to the driving of other process equipment (not shown) such as a gear box for mechanical outputs, and compressors and circulators for the methanol synthesis stage of the process. In practice the air compressor represented at 37 in Figure 2 will comprise two or three stages of compression which may be mounted on a common shaft with the  
10 expander 42 and together with further ancillary equipment drives for the downstream parts of the process.

The process and apparatus described above eliminate the conventional high pressure steam cycle usually included in methanol plants, and thus avoids the  
15 associated expense thereof and the cost of the required water treatment systems and chemicals which are needed to provide a pure feed water for the high pressure steam system. However a source of process steam supplied via line 54 is still required. Nevertheless, this is not high pressure steam and has less rigorous requirements. The steam added via line 54 is required only to be at a pressure which is just above the  
20 reformer pressure and hence the water used to raise such steam does not need to have such a high purity in relation to conventional high pressure steam systems. It is therefore preferred that the process steam is introduced into the feedstock by direct contact of the pressurized natural gas feed with a stream of heated water. Conveniently the water employed is that separated during the cooling of the reformed gas in stage 16,  
25 supplemented as necessary with fresh make-up water. This water may be heated by heat exchange with the reformed gas undergoing cooling in stage 16 and/or by heat exchange with another hot gas stream, for example reacted synthesis gas leaving the downstream methanol synthesis stage 19.

30 Although as described, there are generally significant advantages to be achieved by avoiding the need for a high pressure steam system, in some circumstances it may

be desirable to retain a steam system, and this is contemplated within the scope of the present invention.

Whereas in the foregoing description in relation to the drawings, the  
5 compressed air provided by the compressor 37 constitutes the pressurized oxidant flow delivered to the combustor 34 for burning of the fuel, it will be appreciated that other oxidant flows can be used depending upon the circumstances. Thus the pressurized oxidant flow could comprise air that is either of enriched or depleted oxygen content as compared to atmospheric air, or could in some cases be mostly oxygen. A wide range  
10 of pressurized oxidant flows can be utilized as long as the objective is achieved of providing sufficient oxidant to achieve efficient combustion of the fuel, and provide the required flow of hot combustion products to deliver heat to the reformer.

In another variation of the process and apparatus, heat can be recovered from  
15 the hot reformed gas via gas-to-gas heat exchange. In this arrangement, the pre-reformer (CXP) 14 can be heated directly by part of the flow of hot combustion products in a series or parallel manner as indicated by the broken line 31.1 in Figure 1.

CLAIMS

1. A process wherein a feedstock is subjected to an endothermic reaction with heat required for the endothermic reaction being supplied by heat exchange with a flow of hot combustion products, generated by burning a fuel in a pressurized oxidant flow in a combustion zone, thereby partially cooling said flow of combustion products, and thereafter recirculating part of the partially-cooled flow of combustion products by adding said part to said pressurized oxidant flow before said pressurized oxidant flow enters said combustion zone.
2. A process according to claim 1 wherein the feedstock comprises a gaseous mixture of hydrocarbons and steam which is passed at an elevated pressure over a catalyst to produce reformed gas containing hydrogen and carbon oxides.
3. A process as claimed in claim 1 or 2 wherein said flow of hot combustion products is at a pressure of at least 10 bar gauge.
4. A process as claimed in claim 1, 2 or 3 wherein said flow of hot combustion products is at a pressure of from 5 to 80 bar gauge.
5. A process as claimed in claim 4 wherein said flow of hot combustion products is at a pressure of from 10 to 60 bar gauge.
6. A process as claimed in claim 5 wherein said flow of hot combustion products is at a pressure of from about 20 to about 40 bar gauge.
7. A process as claimed in any one of claims 1 to 6 wherein said flow of hot combustion products is at a pressure that is not more than 10 bar different from the reforming pressure.

8. A process according to any one of claims 1 to 7 wherein 5 to 80% of the combustion products is recirculated.
- 5 9. A process according to any of claims 1 to 8 wherein the amount of combustion products recirculated is such as to provide a flow of said hot combustion products having a temperature within the range of about 1200°C to about 1400°C.
- 10 10. A process according to any of claims 1 to 9 wherein the relative amounts of pressurized oxidant gas and fuel provided to the combustion chamber is such that the hot combustion products existing the combustion chamber have an oxygen content of less than about 2%.
- 15 11. A process as claimed in any one of claims 1 to 10 wherein heating of the feedstock is effected by passing said flow of combustion products in heat exchange relationship to said feedstock.
- 20 12. A process as claimed in any one of claims 1 to 11 wherein the part of the partially-cooled combustion products that is recirculated is further cooled and then repressurized before addition to the pressurized oxidant flow.
- 25 13. A process as claimed in any one of claims 1 to 11 wherein the recycle of the part flow of partially cooled combustion products is effected by means of an eductor wherein the flow of pressurized oxidant gas is passed through a constriction and thence into an expansion zone, whereby a zone of reduced pressure is created, and the part flow of partially cooled combustion products is drawn into this reduced pressure zone to effect the recycle.

14. A process as claimed in any one of claims 1 to 13 wherein the endothermic reaction is effected in two stages comprising a first stage wherein the feedstock is partially reacted by the application of heat thereto and a second stage wherein partially-reacted feedstock delivered from said first stage is further reacted by the application of heat thereto; heating in said second stage being effected by the pressurized flow of hot combustion products; and the reacted gas from the second stage is utilised to effect the heating of the feedstock in said first stage.
15. A process as claimed in any one claims 1 to 13 wherein said reaction is effected in two stages comprising a first stage wherein said feedstock is partially reacted by the application of heat thereto and a second stage wherein partially-reacted feedstock delivered from said first stage is further reacted by the application of heat thereto; heating in both said first stage and in said second stage being effected by said pressurized flow of hot combustion products.
16. A process as claimed in any one of claims 1 to 13 wherein the feedstock is divided into two portions, one of which is reacted in a reaction stage heated by the hot combustion products, while the other portion is reacted in a parallel reaction stage; the reacted gas from the two reaction stages is combined and then subjected to partial combustion with a pressurized oxidant gas and optionally passed through a bed of catalyst; and the resultant hot reacted gas is then used to provide the heat in the parallel reforming stage.
17. A process as claimed in claim 16 wherein the pressurized oxidant gas used for the partial combustion is oxygen or oxygen-enriched air obtained by subjecting compressed air to separation and the residual oxygen-depleted air from the air separation unit is used as the pressurized oxidant gas used to form the hot combustion products.
18. A process as claimed in any one of claims 1 to 17 wherein the portion of the partially-cooled combustion products that is not recycled is delivered to an

expander machine where useful work is recovered from said non-recycled portion by expanding it to a lower pressure and temperature.

19. A process as claimed in claim 18 wherein the useful work is applied to compress a  
5 flow of oxidant to form the pressurized oxidant flow.
20. An apparatus for performing a process wherein a feedstock is subjected to an  
endothermic reaction, said apparatus comprising:
- an endothermic reaction zone;
  - 10 means to deliver a feedstock into said endothermic reaction zone;
  - means to supply a heating medium to said endothermic reaction zone to  
effect said endothermic reaction;
  - a combustion zone;
  - means for delivering to said combustion zone a flow of pressurized oxidant  
15 gas and a supply of fuel;
  - means for burning said fuel in said pressurized oxidant flow in said  
combustion zone to produce a hot flow of pressurized combustion products;
  - means for delivering said hot flow of combustion products to said  
endothermic reaction zone for use as the heating medium therein; and
  - 20 means for recirculating a portion of said flow of combustion products after  
passing through said endothermic reaction zone to said flow of pressurized  
oxidant gas before said flow of pressurized oxidant gas enters said  
combustion zone.
21. An apparatus according to claim 20 for the reforming of a feedstock comprising a  
25 gaseous mixture of hydrocarbons and steam, including means to introduce steam  
into a hydrocarbon stream to form said feedstock, wherein said reaction zone is  
adapted to contain a reforming catalyst.

22. Apparatus as claimed in claim 20 or 21 wherein the means for recirculating a portion of said flow of combustion products includes eductor means having a constriction and an expansion zone; means to pass pressurized oxidant gas through said constriction and thence into said expansion zone, thereby creating a zone of reduced pressure; and means connecting the reduced pressure zone to the part flow of partially cooled combustion products whereby the latter is drawn into the reduced pressure zone to effect the recycle.
- 10 23. Apparatus as claimed in claim 20, 21 or 22 including an expander and means for delivery to said expander as the driving means thereof that portion of said flow of partially-cooled combustion products that is not recycled, said expander being connected in turn to drive a compressor, said compressor comprising means for pressurizing a flow of oxidant gas to form said flow of pressurized oxidant gas.

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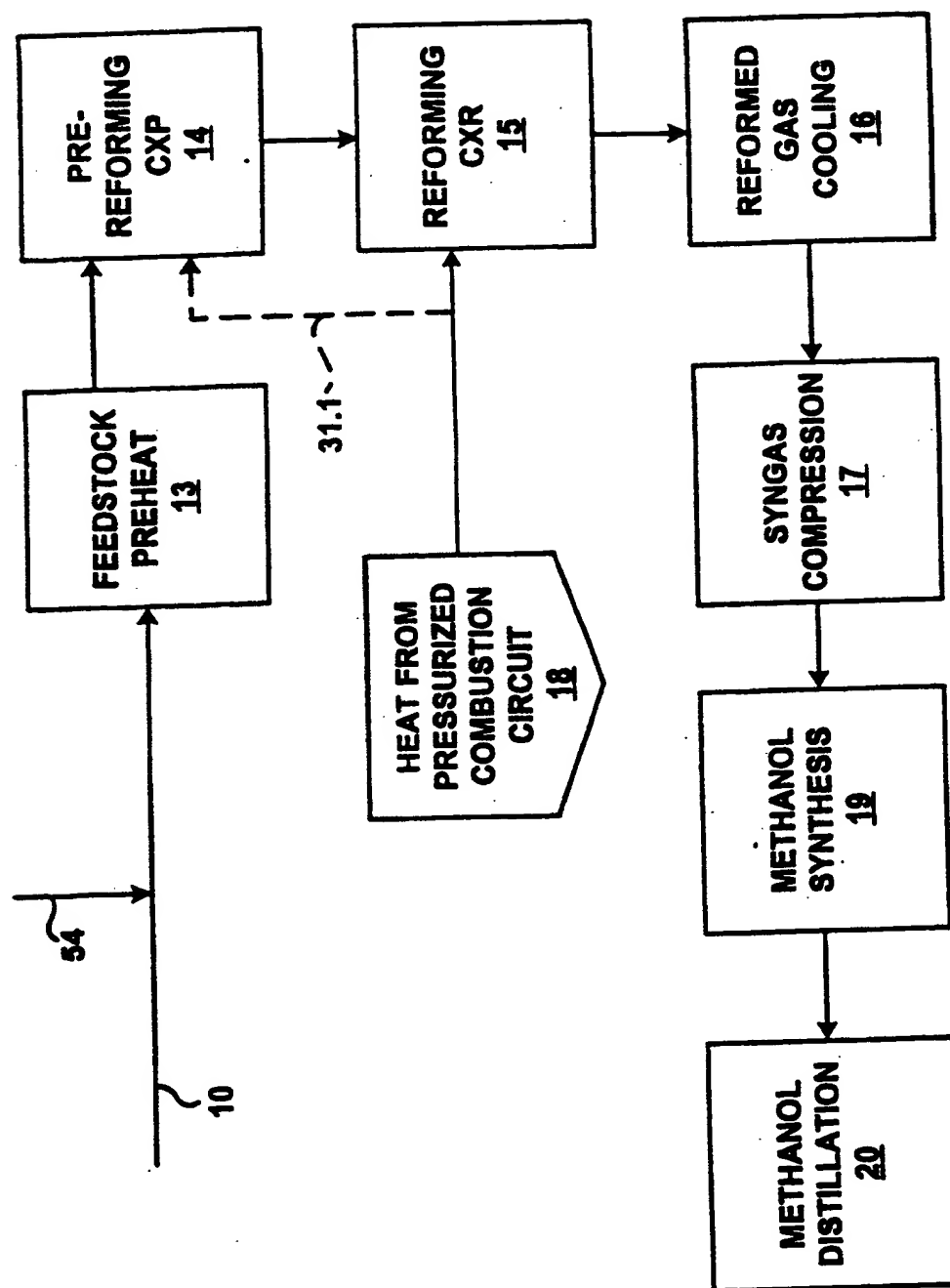


Fig. 1



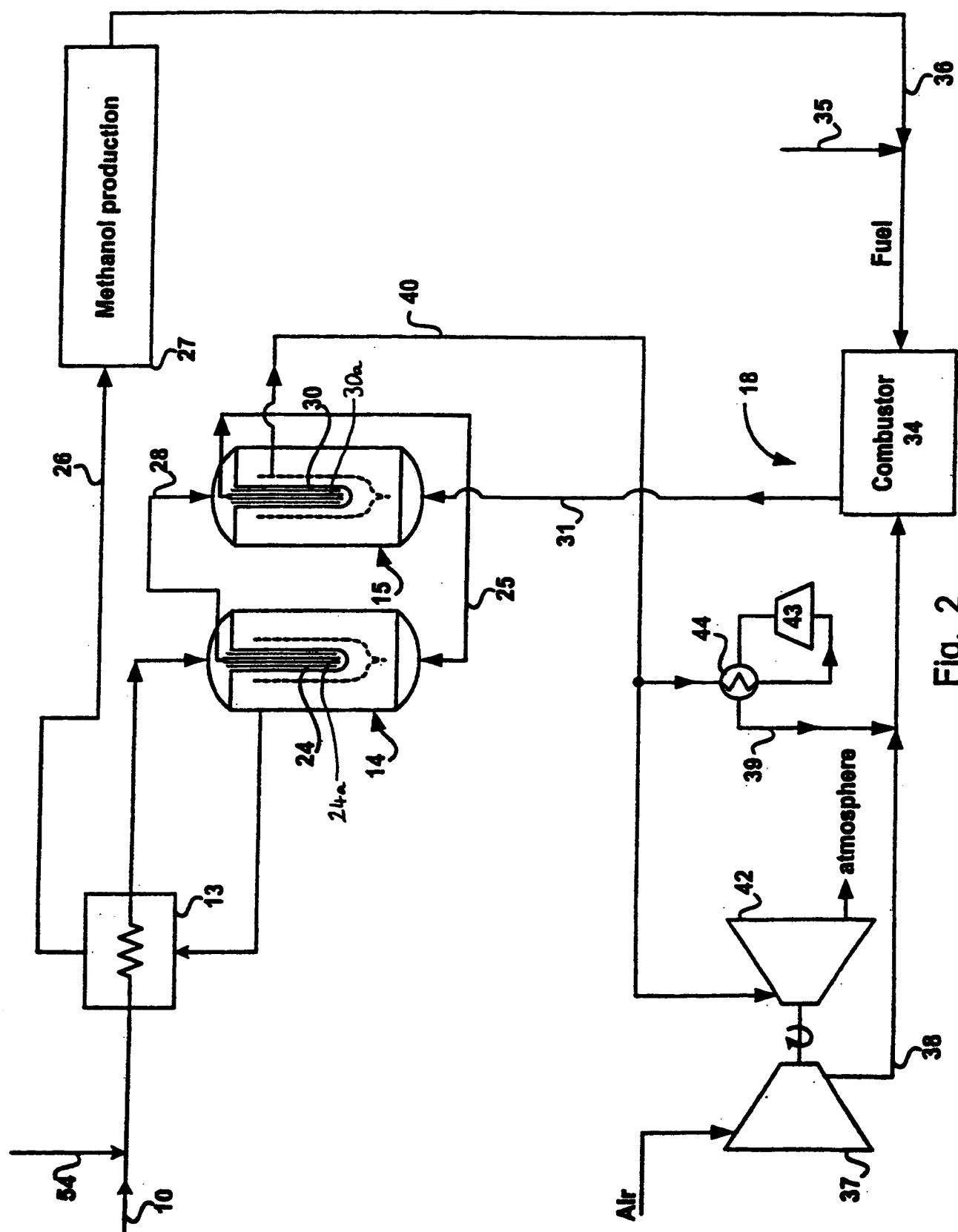
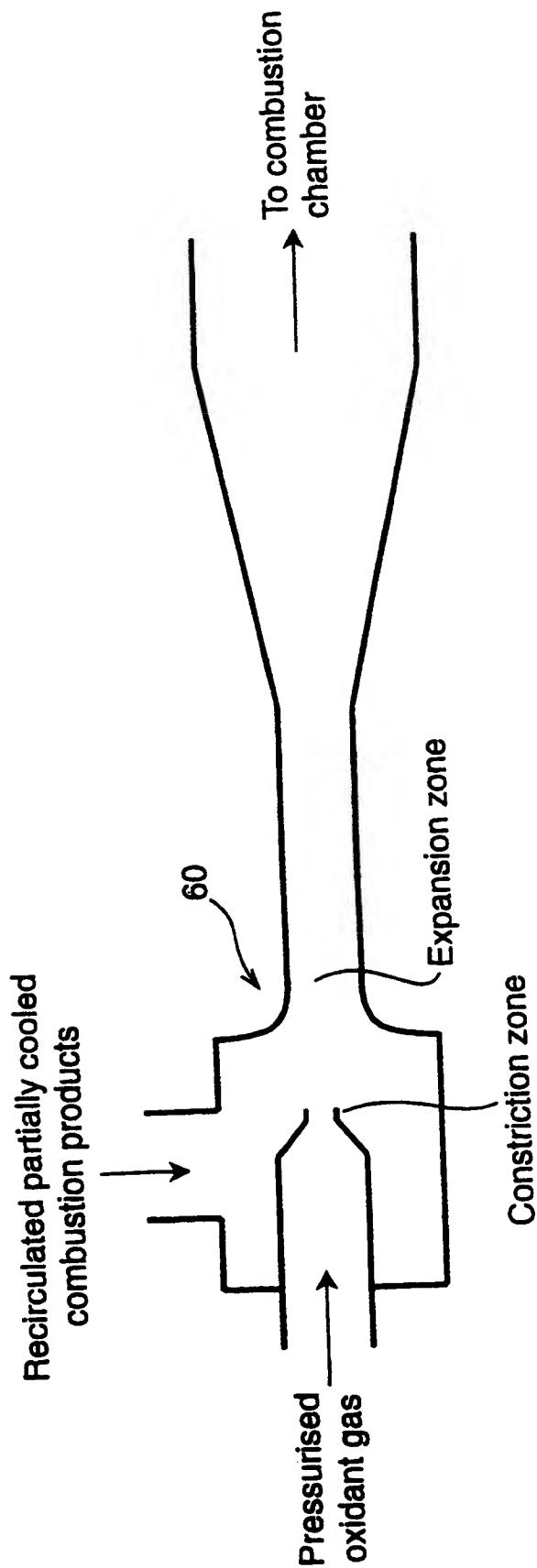


Fig. 2

FIG. 3



## INTERNATIONAL SEARCH REPORT

International Application No

PCT/GB 99/02721

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C01B3/38

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C01B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 212 755 A (SHELL INT RESEARCH) 4 March 1987 (1987-03-04) column 2, line 14 - column 5, line 50 -----	1-8, 11, 20, 21
A	US 5 666 944 A (FERGUSON MARK A) 16 September 1997 (1997-09-16) column 1, line 52 - line 67 -----	1

☐ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

## \* Special categories of cited documents :

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"P" document published prior to the international filing date but later than the priority date claimed

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Date of the actual completion of the international search

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# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/GB 99/02721

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